

**A Facile Wet Synthesis of Nanoparticles of Litharge, the Tetragonal Form of PbO**  
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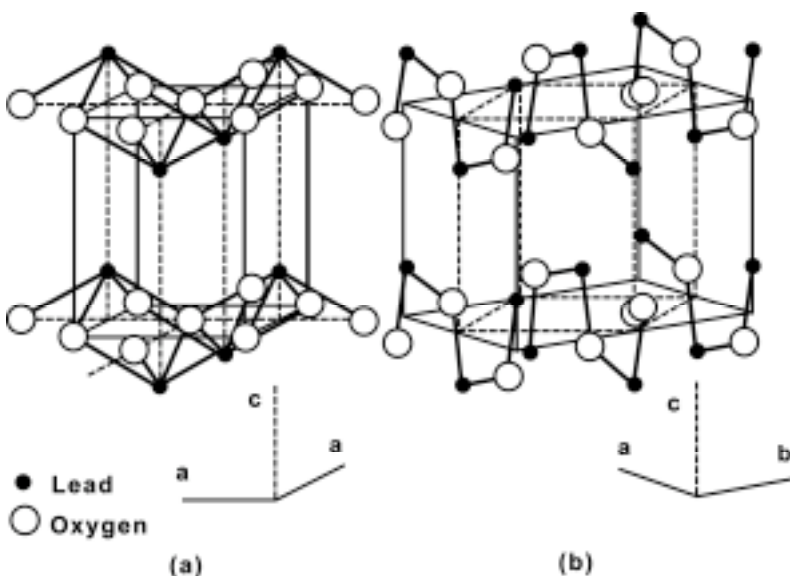
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**ABSTRACT**

The red, tetragonal form of lead oxide,  $\beta$ -PbO, litharge, has been synthesized in the nanoparticle range using a rapid, one-step reaction sequence using water as the reaction medium. The product was characterized by powder x-ray diffraction and scanning electron microscopy. With time at room temperature, the original material slowly changed in color intensity, indicating its alteration to  $\alpha$ -PbO, massicot. Grinding the aged material converted it back to the original litharge form. The role of impurities in the experimental synthesis of the material and microstructural variations in the final product are discussed, along with the PbO-phase compositions of commercial products.

**INTRODUCTION**

Lead(II) oxide exists in essentially two structural polymorphs, with the phase being produced by previous synthetic techniques being dependent on experimental parameters such as temperature,



**Figure 1.** The structures of the  $\beta$ -PbO (litharge) (a) and  $\alpha$ -PbO (massicot) (b) phases of lead(II) oxide. The solid lines represent the unit cell frameworks of the molecules.

pH, and concentration of the lead(II) starting solution. One form is the red tetragonal form,  $\beta$ -PbO, while the other form is the yellow orthorhombic one,  $\alpha$ -PbO (Figure 1). Additionally, microstructural phase changes---ones slightly different from the two principal phases normally reported for the compound---can result as a result of the synthetic route and experimental conditions used to prepare the material. The resulting phase is also partially dependent on contaminant species of various other elements present in the reaction solution in addition to the lead(II) ion itself. Both forms of PbO are photoactive semiconductors with bandgap energies of 1.92 and 2.7 eV for  $\beta$ -PbO and  $\alpha$ -PbO, respectively, and have been discussed with respect both to their use in a variety of applications and their electronic properties [1-3].

The different synthetic approaches to the bulk preparation of lead(II) oxide have been reported in the research literature, with many of them being ambiguous with respect to the exact products formed. All basically concentrate on the use of a starting salt of lead(II) and its reactions with some type of base. Narita *et al* [4] have reported the hydrolysis of lead(II) nitrate with sodium hydroxide, a procedure which results in the formation of both  $\beta$ - and  $\alpha$ -PbO and four different types of lead(II) hydroxide nitrates. A somewhat similar hydrolysis-based reaction sequence used lead(II) alkoxides as the starting material, followed by their aqueous hydrolysis and subsequent dehydration of the resulting complex lead(II) oxide hydrates [5]. A very different approach was the ball milling of  $\text{Pb}_3\text{O}_4$  to form both the  $\beta$ - and  $\alpha$ -PbO forms, with the predominant form of PbO being produced being a function of the length of time of milling [6].

In the present work, nanoparticles of the red, tetragonal form of PbO, litharge, have been synthesized by an easy, quick, reaction sequence using water as the reaction medium by which, unlike previously reported syntheses, the litharge phase is reproducibly formed with no side products or contaminating phases. The product was characterized by powder x-ray diffraction and scanning electron microscopy and compared to published x-ray crystallographic data. Experimental parameters are discussed that lead to both other PbO forms being produced in wet syntheses and to microstructural alterations of both the litharge and other phases.

## EXPERIMENTAL DETAILS

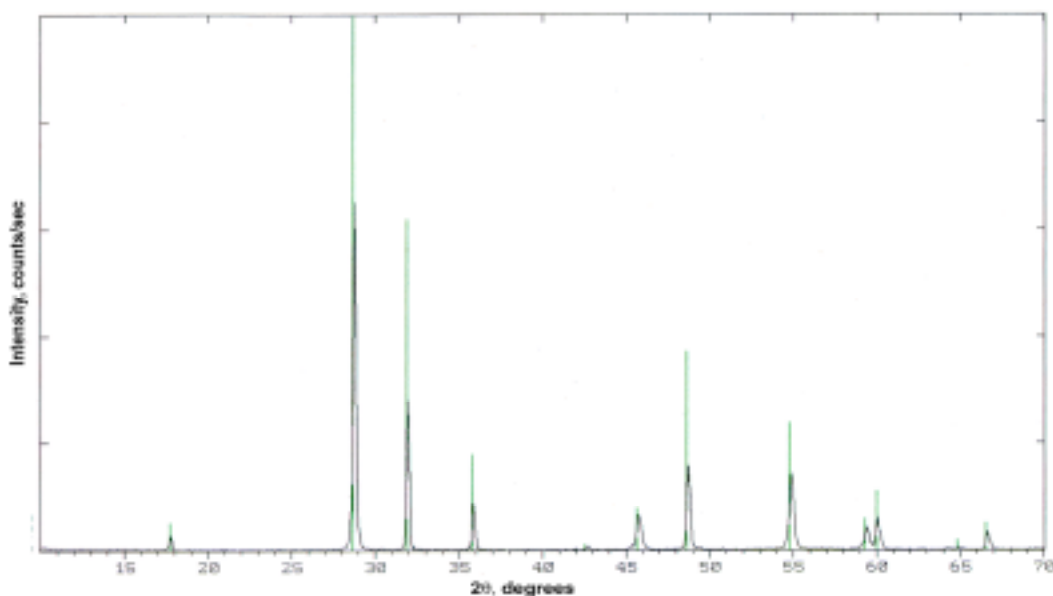
A heated (90°C) aqueous solution (using de-ionized water) of 50 mL of 1.2 M lead(II) acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , (J. T. Baker Reagent Grade) was added to an aqueous solution of 50 mL of 19M NaOH (Fluka) in a Teflon beaker while stirring vigorously. Upon adding the lead(II) acetate, the solution initially became cloudy, then turned a peach color, and finally a deep orange-red. Stirring was stopped, and the precipitate was allowed to settle. The supernatant was then decanted, filtered on a Buchner funnel, washed with de-ionized water, and dried overnight on the filter paper in a drying oven at ~ 90°C. The sample was then removed from the filter paper and lightly crushed in a mortar and pestle. Further grinding resulted in yet smaller particles as described below.

The x-ray powder diffraction patterns were taken on a Siemens Model Daco-MP 5000 Diffraktometer using Cu K $\alpha$  radiation from  $2\theta = 10^\circ$  to  $70^\circ$ . The software is a Siemens Diffract AT software package, Version 3.1. The x-ray powder diffraction file used in the work was Inorganic Phases, Joint Committee on Powder Diffraction Standards (JCPDS)-International Centre for Diffraction Data, Newtown Square, PA. The x-ray powder diffraction pattern for freshly prepared

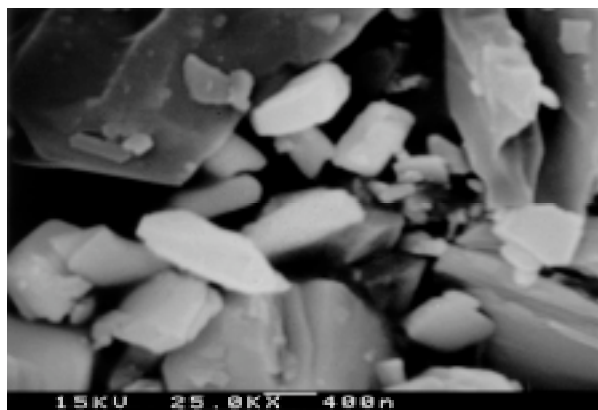
litharge produced a perfect match for the published diffractogram in the database. Scanning electron microscopy was performed using an ISI Model D130-C scanning electron microscope.

## DISCUSSION

The synthetic route used here for the preparation of nanoparticle  $\alpha$ -PbO results in an initially very pure product that separates from the reaction solution almost immediately as very fine crystalline particles that are of nanometer size, both alone and in clusters, during the initial precipitation. Figure 2 shows the x-ray diffractogram of freshly prepared litharge in which litharge is the exclusive, sole product formed. No other complex lead(II) oxide hydrates such as  $3\text{PbO}\cdot\text{H}_2\text{O}$  [7] or  $5\text{PbO}\cdot 2\text{H}_2\text{O}$  [5] were observed in any samples that were isolated.



**Figure 2.** X-ray diffractogram of freshly prepared  $\alpha$ -PbO, litharge.

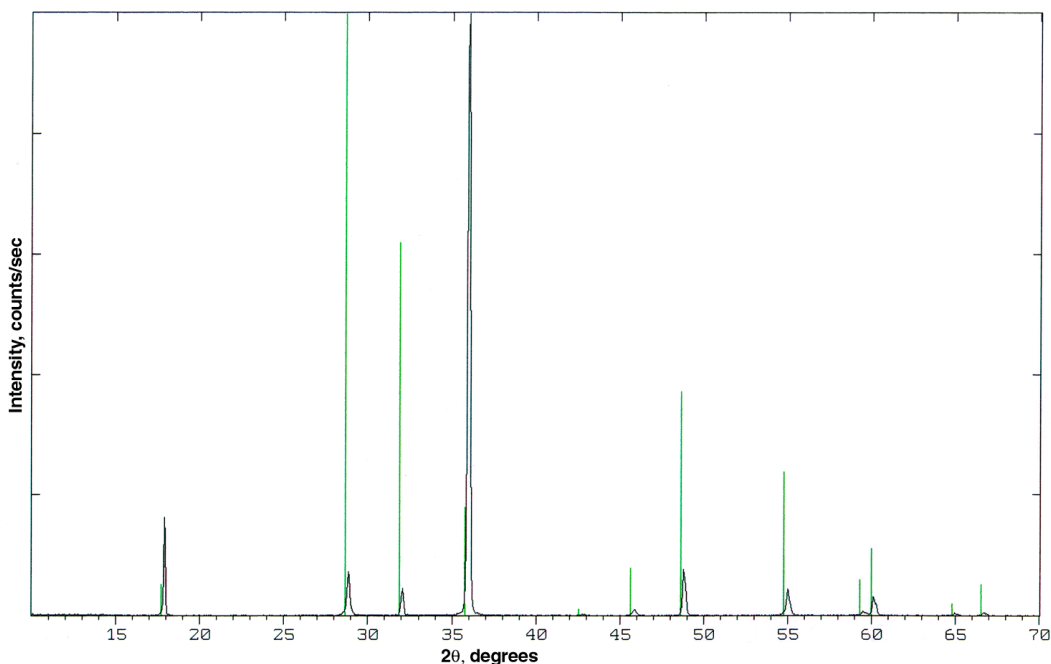


**Figure 3.** Scanning electron micrograph of  $\alpha$ -PbO. The assemblage of different particle sizes shown here was chosen to show both large and small particles before grinding.

Initial gentle grinding in a mortar and pestle produced both the nanometer range size of particles and small clusters of nanoparticles as shown in Figure 3. On standing for a period of several months, the deep red color of the litharge began to turn perceptibly lighter in color,

indicative of its very slow conversion to the yellow massicot form (Figure 4) at room temperature. Further grinding of the litharge, however, accomplished two purposes. First, the small clusters of the litharge were broken into many more single nanoparticles than were formed in the initial precipitation/drying processes. Second, and more beneficially, when samples of the several month-old material that was beginning to convert into massicot were ground, the material was converted back into litharge, with the concomitant change to its original deep red color.

The effects of aging of litharge and its conversion to the orthorhombic massicot form have been previously reported [8]. Additionally, the effects of grinding of  $\beta$ -PbO and its transformation to the  $\alpha$ -form have also been discussed in the research literature [9-11]. Visually perceptible color changes as a function of only very slight structural changes in the  $\beta$ -PbO lattice have also been noted [12] as well as pressure-dependent phases of PbO [13].



**Figure 4.** X-ray diffractogram of aged  $\beta$ -PbO which has begun the process of converting to the  $\alpha$ -PbO form.

Two other issues should be mentioned for researchers involved in the synthetic chemistry and materials science of PbO. First, the importance of the effects of various elemental dopants on the formation of both  $\alpha$ - and  $\beta$ -PbO and their interconversion cannot be overly emphasized. Several studies of this phenomenon have been reported in the literature, including one by Kwestro and Huizing [14]. They addressed the effects of different metal ions and non-metal species such as silicon, phosphorus, and chlorine on which (or mixtures of both, which is very often experimentally observed) of the two forms of PbO are obtained under common synthetic conditions. Isobe and Senna [15] have reported extensive studies of the combined effects of dopants and mechanical activation of litharge and its conversion to massicot.

Finally, one other caveat should be mentioned concerning commercial sources of PbO. Sorrell [16] has noted that the variation in the phase composition of compounds sold as PbO can vary widely. Many commercial sources of PbO use a material, that, because of the bulk industrial processes used to make it, is usually a mixture of both the  $\alpha$ - and  $\beta$ -PbO forms. In one

commercial reagent grade sample he examined, the mixture was 85 % massicot and 15 % litharge. In our research with PbO, we have examined many commercial samples that were specifically denoted as one phase exclusively only to learn from a x-ray diffraction examination that the sample was indeed a mixture. When using either form of PbO in research or application, one must verify the actual form of the material being used.

## CONCLUSIONS

A rapid, easy, reliably reproducible synthetic technique for the preparation of the red tetragonal form of lead(II) oxide,  $\beta$ -PbO, litharge, has been developed which results in the formation of high-purity nanoparticles. The experimental scheme used produces exclusively the tetragonal  $\beta$ -form of the compound with no detectable amounts of the yellow  $\alpha$ -PbO, massicot form. No other side products such as hydrated lead(II) oxides or complex lead(II) salt hydroxides are formed.

## ACKNOWLEDGMENTS

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